

## PATENT SPECIFICATION

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(54) PROCESS FOR COVERING A FIBROUS WEB WITH A  
 POLYMERIC COATING

(71) We, BAYER AKTIENGESSELL-  
 SCHAFT, formerly known as Farbenfabriken  
 Bayer Aktiengesellschaft, a body corporate  
 organised under the laws of Germany, of 509  
 Leverkusen, Germany, do hereby declare the  
 invention, for which we pray that a patent  
 may be granted to us, and the method by  
 which it is to be performed, to be particularly  
 described in and by the following state-  
 ment:—

This invention relates to a process for cover-  
 ing a fibrous web with a polymeric coating.  
 In particular it relates to the coating of leather  
 or the production of imitation leather. The  
 term "imitation leather" is used here to mean  
 a microporous fleece which has a polymeric  
 coating, or covering layer, which is permeable  
 to water vapour.

It is known to bond fibre fleeces by impreg-  
 nating them with polymer solutions or dis-  
 persions and then coagulating the polymer. A  
 porous fleece which "breathes" is thus ob-  
 tained. If this fleece is bonded to a covering  
 layer, a synthetic leather is obtained which  
 has good permeability to water vapour com-  
 bined with a low capacity for absorbing water  
 vapour (see C. L. Nottebohm, *Chemiefasern*  
 9 (1968), page 673 or G. Reich, "Das Leder"  
 17 (1966), pages 261 to 272 or L. Seligs-  
 berger J. Am. Chem. Leather Chem. Assoc.,  
 60 (1965) pages 408 to 419). Such a material  
 is not very suitable for use, for example, as  
 shoe uppers because it is not capable of  
 absorbing and retaining sufficient water.

Fleece bonding agents which provide for  
 high water uptake of the fleece and for good  
 permeability to water vapour are known *per se*.  
 Ionic polyurethanes are particularly suitable  
 for this purpose, especially ionic polyurethane  
 latices of the type described e.g. by D. Diete-  
 rich, W. Keberle, and H. Witt, *Angew. Chem.*

82 (1970 pages 53 to 63). Hydrophilic  
 binders, such as products which contain poly-  
 vinyl alcohol or polyethylene glycol are also  
 suitable for this purpose.

In bonding a microporous covering film to  
 a microporous fleece (i.e. a fleece which is  
 permeable to water vapour) however, the  
 porosity is often lost to a large extent be-  
 cause many of the pores get blocked.

The present invention provides a process  
 for covering a fibrous web with a polymeric  
 coating comprising the steps of:—

- a) applying to a temporary support a layer  
 of a reaction mixture which comprises  
 (1) at least one polyisocyanate and (2)  
 at least one compound containing active  
 hydrogen atoms and which will undergo  
 a polyaddition reaction with the polyiso-  
 cyanate to form a microporous poly-  
 urethane (urea) layer,
- b) applying to the layer, before the poly-  
 addition reaction is complete, a fibrous  
 web, and
- c) removing the fibrous web with the adher-  
 ing polymeric layer from the temporary  
 support.

The fibrous web can be a woven or knitted  
 fabric or natural leather, in particular split  
 leather, grain leather or suede. It will be  
 appreciated that such leathers are sufficiently  
 fibrous in nature to allow them to be used in  
 the process according to the invention.

In a preferred embodiment the fibrous  
 web is a fibre fleece and the finished product  
 (fibre fleece with polymeric coating) has  
 utility as imitation leather.

In a particularly preferred embodiment the  
 fibrous web is an unbonded fibre fleece and  
 after it has been applied to the layer and  
 before the step (c) the fleece is impregnated  
 with an aqueous solution of a polymeric binder

and the binder is coagulated, the amount of binder used being 10 to 98% by weight based on the weight of the fibre fleece. This eliminates one working step as bonding of the fleece and formation of the covering layer are carried out almost simultaneously.

Because the fibrous web is applied to the layer while it is still soft and reacting the penetration of the fibres into the layer is good and the bonding excellent. Furthermore the process preserves the micro porosity of the fibrous web.

The support used is a temporary support and the final product is removed therefrom. This means that the support is made preferably from a solid material which is inert to polyurethane-(ureas) the reactive mixture forming the polyurethane-(urea), and any solvents present, and provided such material does not stick or adhere to the polyurethane or -(urea).

The reaction mixture for the production of the polymeric coating are preferably solutions of compounds which are capable of polyaddition and which form microporous polyaddition products after polyaddition and removal of the solvents. Solutions of this kind have been disclosed e.g. in Belgian Patent Nos. 715,003; 705,612; 719,272 and 725,052. (As is customary in the art the reaction of, for example, a polyol and a polyisocyanate to give a polyurethane is called a polyaddition reaction). Furthermore for brevity the term "polyurethane" will be used in its wider sense as meaning polyurethane(urea), i.e. it encompasses polyurethanes, polyureas and mixed polyurethane-polyureas.

The starting materials for such a process are already known. Polyisocyanates (particularly diisocyanates) are used as the compounds which contain NCO groups. Compounds containing active hydrogen atoms usually contain OH or NH groups. Compounds which contain NH<sub>2</sub> groups are amines, aminoalkanol and hydrazine and its derivatives. Suitable compounds which contain OH groups are low molecular weight (e.g. 18—1250) and high molecular weight (e.g. 1250—3500) glycols, polyethers, polythioethers, polyesters, polyether esters, polyacetates, polyester amides and polysiloxanes.

Generally it is preferred to use (1) at least one polyisocyanate (2) at least one compound containing NH and/or OH groups which will react with NCO groups and having a molecular weight of at least 500 and (3) at least one chain lengthening agent which has a molecular weight below 500 and NH and/or OH groups which will react with NCO groups.

These compounds are preferably reacted with each other by a single stage process or a two-stage process,

#### 1. Single stage process

If the active hydrogen-containing reactants are not substantially different from each other in their reactivity towards isocyanate, it is advantageous to employ the single stage process. In this process, the reactants (1), (2) and (3) are mixed together without any previous reaction preferably in solvent and are converted into the microporous polyurethane.

Preferably the components containing OH groups and, if desired, NH groups are dissolved in the solvent or solvent mixture, the polyisocyanate, if desired, also in solution, is stirred in at the required temperature, and catalyst is added to the mixture if desired. The heat released by the polyaddition reaction raises the temperature of the solution. Clouding of the solution accompanied by an increase in viscosity generally occurs after some time. The solution is then poured out on to the temporary support. The solution starts to gel within 20 minutes. One may, of course, use reaction mixtures which have longer gelling times but this is not of great practical interest. The polyaddition reaction is advantageously completed on the support at a drying cupboard temperature of more than 60°C. with solidification of the film, and the solvent evaporates off at the same time and/or afterwards. Lower temperatures may be employed, but the reaction time is then longer.

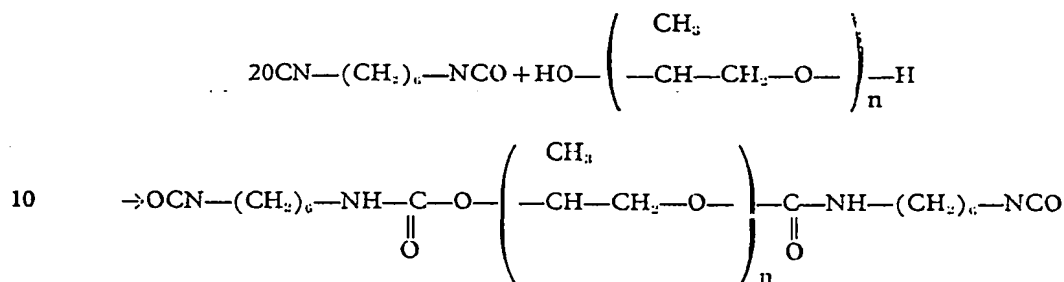
In the single stage process, the reactivity of the higher molecular weight compounds which have at least two terminal OH groups towards isocyanates should not differ substantially from the reactivity of the cross-linking agent towards isocyanate. The reactivities are preferably about equal but the reactivity of the cross-linking agent may be greater or less by a factor of up to about 5 and preferably not more than 2. By reactivity is meant the reaction velocity constant in 1/mol sec. (see J. H. Saunders and K. C. Frisch "Polyurethanes" I, New York (1962), pages 206 to 208).

#### 2. Two stage process

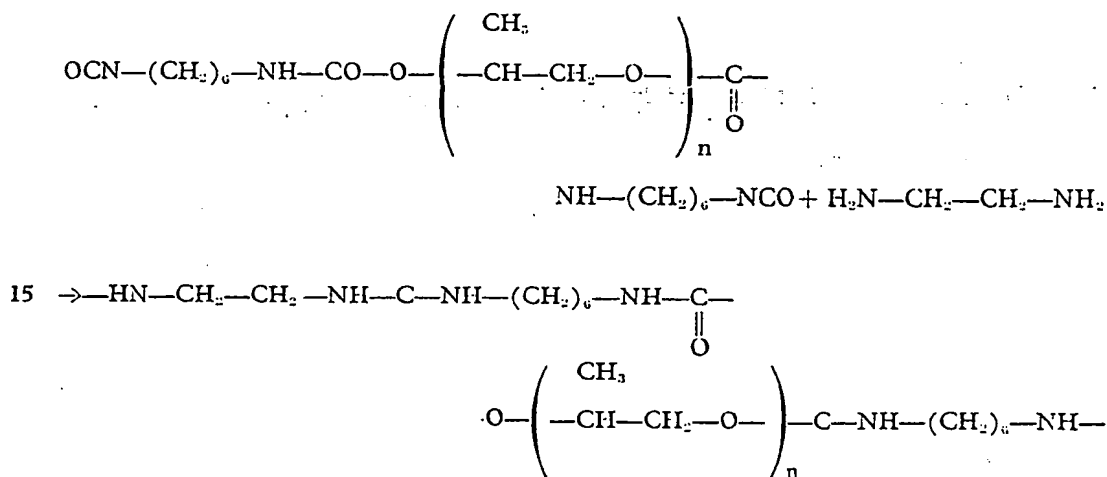
If the active hydrogen-containing reactants differ substantially from each other in their reactivity, the more reactive compounds would first react with each other and they would form sparingly soluble compounds in the organic solvent, which would precipitate and interfere with the formation of polyurethane. This is particularly the case when compounds which contain highly reactive hydrogens, especially amines, and compounds which contain OH groups are to be reacted with polyisocyanates. A two-stage process is therefore used in such cases, the compounds which contain OH groups, for example, are reacted in a first stage with excess polyisocyanate to form a so-called prepolymer. The prepolymer is then reacted with the more reactive compound in the organic solvent in a second stage.

Usually reactants (1) and (2) are reacted to give the prepolymer which is subsequently mixed with the chain lengthening agent (3) in a second stage.

In the simplest case, a polypropylene glycol ether, for example, is reacted with a diisocyanate, e.g. hexamethylene diisocyanate, to form the prepolymer:



In the second stage, the prepolymer is reacted with a diamine, e.g. ethylene diamine, to form a high molecular weight microporous polyurethane polyurea:



Preferred starting materials (2) for use in the process according to the invention are compounds of molecular weight above 500 which contain at least two terminal OH groups, for example polyethers, polyesters, polycarbonates, polyacetates, polyesteramides, polythioethers or polysiloxanes. Compounds of this type have been described, e.g. in J. H. Saunders and K. C. Frisch "Polyurethanes" I, New York (1962), pages 32 to 61 and in the literature cited there.

Especially to be mentioned are the polyesters of dicarboxylic acids, such as phthalic acid, terephthalic acid, sebacic acid or preferably adipic acid and dialcohols or mixtures of dialcohols, e.g. ethylene glycol, propylene glycol, butane-1,4-diol, hexane-2,5-diol, 2,2-dimethylpropane-1,3-diol, hexane-1,6-diol, 2-methylhexane-1,6-diol, 2,2-dimethylhexane-1,3-diol, p-bis-hydroxymethylcyclohexane, 3-methyl-pentane-1,4-diol or 2,2-diethylpropane-1,3-diol, and preferably diols or mixtures of diols which contain 5 or more carbon atoms

because polyesters of this type have a relatively high resistance to hydrolysis and, especially if diols which have alkylene radicals in the side chains have also been used, the end products have a satisfactory elasticity at low temperatures. Polyesters obtained by the polymerisation of caprolactone with diethylene glycol having a narrow molecular weight distribution are also suitable starting materials. The polyesters which are obtained from diphenylcarbonate and glycols are particularly suitable.

Polyurethanes and polyurethane-ureas which have excellent resistance to hydrolysis can be obtained from polyalkylene ethers such as polypropylene glycols. Polytetramethylene ether diols are especially advantageous for this purpose and may be used either as such or in the form of mixed polyethers.

The process according to the invention can surprisingly also be carried out with polyhydroxyl compounds which are miscible with water, e.g. polyethylene glycol ether diols, in

which case polyurethanes with a high water uptake capacity are obtained.

Polyols, amino-alcohols and polyamines may be mentioned as examples of low molecular weight chain lengthening agents (3) which contain at least two OH or NH groups.

The chain lengthening agents should have a molecular weight of from 18 to 500, preferably 32 to 350. Apart from water, the following are examples of suitable chain lengthening agents, which can be used either separately or as mixtures: ethylene glycol, propylene glycol, butane-1,4-diol, hexane-1,6-diol, hydroquinone-bis-( $\beta$ -hydroxy-ethylether), p-xylyleneglycol, ethylene-diamine, propylene-1,2- or -1,3-diamine, tetramethylene-1,4-diamine, hexamethylene-1,6-diamine, 2,2,4-trimethylhexane-1,6-diamine, 1-methyl-cyclohexane, 2,4-diamine, 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane, 4,4'-diamino-dicyclohexylmethane, bis-(aminopropyl)-piperazine or aromatic diprimary amines such as 4,4'-diamino-diphenylmethane, bis-2,2-(4-aminophenyl)propane, 4,4'-diamino-diphenylsulphide, 4,4'-diamino-diphenylether, 1-methyl-2,4-diaminobenzene or araliphatic diprimary diamines such as m-xylenediamine,  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-p-xylene diamine, 1,3-bis-( $\beta$ -aminoisopropyl)-benzene, diamines which contain sulphonic acid groups, e.g. 4,4'-diamino-stilbene-2,2'-disulphonic acid or 4,4'-diamino-diphenylethane-2,2'-disulphonic acid, ethylene diamine-N-butylsulphonic acid, hexamethylene-1,6-diamine-N-butylsulphonic acid, 1,6-diaminohexamethylene-3-sulphonic acid or their alkali metal salts, hydrazines such as carbodihydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide and addition products of ethylene oxide and propylene oxide with ammonia or aliphatic or aromatic amines, e.g. diethanolamine, triethanolamine or methyl- or phenyl-diethanolamine, which increases the dyeability of the products of the process; furthermore, hydrazine, e.g. also in the form of hydrazine hydrate, methylhydrazine and dihydrazines such as N,N'-diamino-piperazine.

Secondary diamines may also be used, preferably those which have a symmetrical structure such as piperazine or 2,5-dimethylpiperazine or 3,3'-dichloro- or 3,3'-dimethyl-4,4'-di-(methylaminophenyl)methane.

The usual polyisocyanates (described for example by W. Siefken, Liebigs Ann. Chem. 562, pages 75 to 136 (1949)) or higher molecular weight (above about 500) reaction products which contain at least two NCO groups per molecule (so-called prepolymers having an NCO:OH ratio  $\geq 1.2$ ) obtained from the above mentioned polyhydroxy compounds with an excess of polyisocyanates are suitable for the process. Suitable polyisocyanates for the process are particularly aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic

diisocyanates or mixtures thereof. Particularly to be mentioned are diisocyanates which have a symmetrical structure, e.g. diphenylmethane-4,4'-diisocyanate, diphenyl-dimethylmethane-4,4'-diisocyanate, 2,2',6,6'-tetramethyl-diphenylmethane-4,4'-diisocyanate, phenylene-1,4-diisocyanate, diphenylether-4,4'-diisocyanate or their alkyl-substituted, alkoxy-substituted or halosubstituted derivatives, as well as tolylene-2,4- and 2,6-diisocyanate and their commercial mixtures, 2,4-diisopropylphenylene-1,3-diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate and  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-p-xylylene diisocyanate, alkyl or halosubstitution products of the above diisocyanates, e.g. 2,5-dichloro-p-xylylene diisocyanate or tetrachloro-p-phenylene diisocyanate, dimeric tolylene-2,4-diisocyanate, bis-(3-methyl-4-isocyanato-phenyl) urea or naphthalene-1,5-diisocyanate. Aliphatic diisocyanates such as hexane-1,6-diisocyanate, cyclohexane-1,4-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1-isocyanato-3-isocyanato-methyl-3,5,5-trimethylcyclohexane or 2,2,4-trimethylcyclohexane-1,6-diisocyanate are employed to give products which undergo very little discolouration on exposure to light. Diisocyanates such as  $\omega,\omega'$ -di(isocyanatoethyl)-benzene or 1,2,3,4,5,6-hexahydro-di-phenylmethane-4,4'-diisocyanate also yield products which undergo little discolouration in the light.

On account of their commercial availability and their properties, the diisocyanates preferably used are diphenylmethane-4,4'-diisocyanate, the isomeric tolylene diisocyanates and in some cases hexane-1,6-diisocyanate and dicyclohexylmethane-4,4'-diisocyanate.

In the two stage process, polyhydroxyl compounds having molecular weight above 500 (2) are preferably reacted with diisocyanates (1) in a molar ratio of about 1:1.25 to 1:4.0, if desired in several stages, e.g. in solvents which are inert to isocyanates, such as tetrahydrofuran, dioxane or chlorobenzene, and at temperatures of about 40°C. to 130°C., preferably 70°C. to 100°C. The reaction times used are such that a substantially linear prepolymer with terminal NCO groups is obtained. By reacting approximately equivalent quantities of bifunctional chain lengthening agents (3) with this prepolymer a substantially linear elastomeric polyurethane or polyurethaneurea is obtained.

With polyhydroxyl compounds (2) of lower molecular weight, e.g. 750 to 1250, the reaction with the diisocyanates (1) is advantageously carried out with lower NCO/OH ratios, e.g. 2.0:1 to 1.25:1, whereas with polyhydroxyl compounds of higher molecular weight, e.g. 1700 to 2500, high NCO/OH ratios are preferably employed, e.g. 3:1 to 1.65:1.

When using such higher molecular weight

polyhydroxyl compounds, a certain amount of low molecular weight diols (molecular weight preferably below 250), e.g. ethylene glycol, butane-1,4-diol, bis-N,N-( $\beta$ -hydroxy-ether) methylamine, bis-N,N-( $\beta$ -hydroxypropyl) methylamine, N,N'-bis-hydroxyethyl piperazine or hydroquinone-bis-( $\beta$ -hydroxyethyl-ether) are preferably included, for example 10 to 300 mols percent and preferably 20 to 100 mols percent of the OH content of the higher molecular weight polyhydroxyl compound. Diols which have tertiary nitrogen are particularly effective for increasing the dyeability and improving the light fastness and they provide additional points for subsequent after treatments such as cross-linking e.g. with compounds which have a strong alkylating action such as 4,4'-dichloromethyldiphenylether.

The quantity of NCO groups in the prepolymers (based on the solvent-free prepolymer) influences the properties of the polyurethanes obtained from the prepolymers. It should be at least 0.50% by weight and should preferably be between about 1.00 and about 7.6% by weight and in particular between about 1.5 and 4.0% by weight in order to produce polyurethanes which have sufficiently high melting points, tear resistance, elongation at break and stress values. If water is used as chain lengthening agent, the NCO content is preferably higher, e.g. between 3.5 and 7.6 percent by weight, because a portion of the NCO groups is theoretically first saponified to form amino groups.

It is usually preferred to have solvent present in the reaction mixture. The solvents used for the process according to the invention are preferably organic compounds which are liquid under the reaction conditions and have a boiling point below 250°C. and which do not react with the starting materials under the reaction conditions. Suitable solvents are e.g. aliphatic hydrocarbons such as pentanes and hexanes and the homologous, optionally alkylated cycloalkanes such as cyclohexane, methylcyclohexane or cyclododecane; petroleum hydrocarbon fractions, especially mixtures of aliphatic hydrocarbons having boiling points between 80°C. and 250°C., e.g. ligroin, cleaning petrol, mineral spirits, mepasin, oil of turpentine, mixtures of aliphatic and aromatic hydrocarbons such as tetralin and decalin, aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, diethylbenzene and mesitylene and chlorinated hydrocarbons such as di-, tri-, and tetrachloromethane, di-, tri- and perchloroethylene, di-, tri-, tetra-, penta- and hexa-chloroethane, 1,2- and 1,3-dichloropropane, isobutylchloride, dichlorohexane, chlorocyclohexane, chlorobenzene and chlorotoluene, ethers such as di-n-propylether, di-i-propylether, di-n-butylether, ethylpropylether, anisole, phenetole, esters such as diethyl- and dimethyl-carbonates, ethyl, propyl, butyl, amyl and hexyl acetate, methoxybutylacetate,

methyl propionate, ethylpropionate, methyl glycol acetate and dimethyloxalate and ketones such as acetone, methyl ethyl ketone, methylisobutyl ketone, methoxyhexanone, mesityl oxide, phorone and cyclohexanone.

The reaction between the starting materials may be catalysed with the known isocyanate polyaddition catalysts (see J. H. Saunders and K. C. Frisch "Polyurethanes" I, New York (1962) page 212). Volatile tertiary amines are preferably used because these are known to have the least deleterious effect on the resistance of the end products to hydrolysis.

In order to produce microporous products a non-solvent for the polyurethane (urea) produced is preferably present. Preferably the following conditions should also be observed:—

- 1) Polyaddition is carried out in a solvent or mixture of solvents in which the starting materials for polyurethane synthesis are soluble at the reaction temperature;
- 2) The solvent or solvent mixture must not cause noticeable swelling of a homogeneous non-porous film of this polyurethane;
- 3) The quantity of solvent must not exceed the maximum quantity which the polyurethane is capable of enclosing as internal phase during its preparation. In the course of the reaction, the polyurethane becomes insoluble in the solvent with progressive formation of the polyurethane, so that pores are obtained after removal of the solvent.

The solvent used preferably only swells the finished polyurethane to the extent that when a sample of the homogeneous polyurethane film, e.g. in the form of a disc 3 mm in diameter and 0.2 to 0.5 mm in thickness is placed in the solvent, it absorbs less than 50% of its own weight in 24 hours by swelling. Mixtures of such non-swelling solvents may, of course, also be used. In addition, the mixture may contain solvents which swell the polyurethane to an extent of more than 50% or even dissolve the polyurethane. Such solvents, however, must have not more than half the evaporation time of the other, non-swelling solvents so that on drying they evaporate more quickly than the non-swelling solvents. The evaporation time may be determined according to DIN 53 170. If these conditions are not met, non-porous material may be obtained. In practice, however, it has been found that minor quantities of polyurethane solvents which have a higher vaporisation temperature than the other solvents may be satisfactorily included to improve the flow of the end products without the microporosity being thereby impaired. The addition of very polar solvents in quantities of up to 100% (based on the polyurethane which is to be formed) but preferably 5 to 80% provides a better levelling effect when the films are being formed. Examples of such very polar

solvents are N,N-dimethylformamide, N,N-dimethylacetamide, trichlorobenzene, dimethylsulphoxide, tetramethylurea and camphor.

5 The quantity of solvent used is an important factor in determining the porosity of the product. As the quantity of solvent is increased, the permeability to water vapour passes through a maximum.

10 The maximum quantity of solvents used for the preparation of the polymeric layer is determined by the capacity of the polyadducts to disperse such solvents. The quantity of solvents actually used may be 30 to 100% and preferably 50 to 98% of the maximum quantity, depending on the lyophilic character of the starting materials, the reaction temperature and the composition of starting materials. Films of different porosity can be obtained by varying the quantity of solvents within the range.

20 The preparation of a solution of starting materials at a concentration of less than 10% by volume is of little practical significance because if the solution is too dilute phase separation often occurs as polyaddition progresses and moreover the solvent often separates in the form of a serum after the shaping process.

25 On phase reversal, i.e. when the polyurethane is no longer capable of dispersing the solvent but becomes dispersed in the solvent, porous products which are unsatisfactory in their appearance for their intended application are frequently produced.

30 The permeability to water vapour can therefore easily be adjusted to the desired value by carrying out a series of tests with increasing quantities of solvent and measuring the porosity of the resulting films. The quantity of solvent required for any given permeability to water vapour can then be easily read off a graph in which the permeability to water vapour is plotted against the quantity of solvent.

35 Any fibre fleece which can be produced by known methods is suitable for use in the process. Suitable methods for producing fleeces are, for example, the methods used for producing crimped fleeces, pneumatic methods, methods for producing spun fleeces or the wet methods, e.g. for fleeces produced in a paper making machine. Woven and knitted fabrics and natural materials such as split leather are suitable with certain reservations. The fleece is best applied to the polymeric coating while the coating still contains more than 50% of the original quantity of solvent. Preferably the fleece is placed onto the polymeric coating while the coating is still capable of deformation so that the fleece sinks into the covering layer to a certain extent, i.e. it penetrates 1 to 80% of the thickness of the covering layer, preferably 10 to 30% of the thickness. To achieve this, the unbonded fleece is preferably applied within a time which is 0 to 300

times, preferably 1 to 100 times and especially 15 to 50 times the reaction time of the reaction mixture. The "reaction time" of the reaction mixture is the length of time after the reactants have been mixed (or treated with catalyst) during which the solution can still be stirred. In other words, it is the time during which the reaction solution is still reversibly mechanically deformable. After cloudiness has appeared in the reaction mixture, the solution is poured on to the temporary support and the fleece is then applied, preferably within 1.5 to 50 times the reaction time. In the two stage process cloudiness generally occurs after addition of the chain lengthening agent (generally a polyamine) to the prepolymer solution. In the single stage process cloudiness generally occurs after the addition of catalyst to the solution which contains the higher molecular weight component which contains at least two OH groups (e.g. polyester), polyol (e.g. butane-diol and polyisocyanate) (e.g. 4,4'-diisocyanato-diphenylmethane). Polyaddition is then completed as the solvent evaporates. Polyaddition and evaporation of the solvent are preferably completed at 20 to 200°C., more preferably at 60 to 150°C., and most preferably at 80 to 120°C.

The fleeces may be made of polyester, polyamide, polyacrylonitrile, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol, cotton, staple rayon, collagen, regenerated cellulose or polyurethane fibres or mixtures of these fibres. Bonding with the aqueous dispersion preferably takes place mainly after completion of the polyaddition and removal of the solvent.

If desired the temporary support can be shaped so that the fibrous web when removed will be correspondingly shaped. Thus it is possible to make shoe or boot uppers having decorative seams or perforations.

Furthermore if desired the temporary support may be coated with a finish before the layer of reaction mixture is applied. The finish adheres to the polymeric coating and is removed in step (c) from the temporary support.

Such a process can be carried out as described below.

1) A very thin film of finish (e.g. 5 to 20  $\mu$ ) is applied to a temporary support, e.g. a separating paper, a support which has been coated with a layer of polyolefine, silicone or perfluoroalkylated coating, a steel strip or a silicone rubber sheet. For example a silicone rubber mould or sheet can be used the surface of which represents the negative image of an object, e.g. the surface of grain leather or a boot upper having decorative seams or perforations. (If such a matrix is used, the final product obtained will show all the details of the object the matrix was taken from). Suitable polymers for their pur-

pose are e.g. polyurethane latices of the type described by D. Dieterich et al in Agnew. Chem. 82 (1970) Pages 53—63 and in the literature cited there or a polyacrylate, in other words a product of the type suitable for finishing leather.

2) After drying, a microporous layer is produced from the reaction mixture using the single stage or two-stage process.

3) The fibre fleece, generally an unbonded fleece, or other fibrous web is applied within 0 to 3000 times the reaction time.

4) Polyaddition is completed and the solvent evaporated at a temperature of 20°C. to 200°C.

5) After 10 to 600 minutes, the product is removed from its temporary support.

6) The fleece is bonded with the aqueous polymer dispersion.

7) If desired, the imitation leather is embossed.

8) If step 1) has been omitted, the completed product may then be treated with a finish.

If in step 3, a substrate other than an unbonded fleece is used, step 6 is omitted.

The microporous layer 2) may be produced by the single stage or the two-stage process as above.

The composition of starting materials for the polyurethane should preferably be such that the polyurethane produced has a Shore A hardness of more than 50 kg wt/cm<sup>2</sup> and a softening range above 100°C. and preferably above 130°C. when in the form of a homogeneous, non-porous sheet. The Shore A hardness is determined according to DIN 53505. The softening range may be determined in known manner, e.g. on a Kofler block (see Houben-Weyl (1953) "Analytische Methoden" 789, 792).

Suitable formulations for polyurethanes may be found in the technical literature on the subject, e.g. E. Müller et al "Angewandte Chemie" 64 (1952) 523—531. If it is intended to use formulations whose properties have not yet been described, it is advisable to prepare the polyurethane in bulk by the melt casting process or in dioxane and to investigate its properties.

Polyurethanes which have the properties mentioned above may be obtained, for example, from:

1) 1 Mol of a linear or slightly branched compound which contains OH end groups and has a molecular weight of 1500 to 2500.

2) 0.5—4 mols of a conventional polyurethane chain lengthening agent.

These compounds are reacted with the polyisocyanate in the solvent mixture preferably at a concentration of 10 to 100% and for microporous sheets most preferably 20 to 60%. Higher proportions of polar compounds require higher quantities of solvent.

In order to obtain a film with good microporosity, it is necessary that the reaction mixture should gel soon after it has been cast. Gelling is a gel-like solidification of the reaction mixture without phase separation, i.e. without serum-like separation of solvent. Once gelling has occurred, the sheet structure generally can no longer be deformed. Progressive solidification occurs after gelling due to the progressive polyaddition.

The process admits of the addition of other polymers, dyes, fillers, stabilizers, cross-linking agents etc. in the form of solutions, organic dispersions or solids which are advantageously incorporated in the starting solutions.

Known substances may be used as binders for the fleeces, for example copolymers of butadiene with styrene, acrylonitrile and/or (meth) acrylic acid, polychloroprene, (meth) acrylic acid ester copolymers which if desired have been mixed with heat sensitizing agents prior to coagulation (see French Patent No. 1,381,222) or mixtures of the type described in Belgian Patent Specification No. 654,817 or binders of the type described in British Patent Specification No. 1,060,785. Polyurethane latices of the type described by D. Dieterich et al in Angew. Chem. 82 (1970) pages 53 to 63 and in the Patent literature cited there have been found to be particularly suitable.

Examples of the preparation of aqueous polyurethane dispersions which are especially suitable for the process may be found in German Auslegeschrift Nos. 1,097,678; 1,187,012; 1,184,946; 1,178,786 and 1,179,363, in Belgian Patent Specification Nos. 653,223; 658,026; 669,954; 673,432 and 688,299, in British Patent Specification No. 883,568, in French Patent Specification No. 1,108,785, in U.S. Patent Specification No. 3,178,310 and in German Offenlegungsschrift No. 1,939,911.

Dispersions which have been prepared without the use of emulsifiers are especially suitable for the process according to the invention, and particularly emulsifier-free dispersions of anionic polyurethane which have sulphonate and carboxylate groups as well as dispersions of this type of cationic polyurethanes which have quaternary ammonium groups.

Dispersions of polyurethanes with anionic groups are generally prepared by reacting the prepolymer which contains isocyanate groups with the anionic component, preferably in solution in an organic solvent, adding water and then distilling off the organic solvent if desired. If desired, the process may be reversed, in which case water containing the anionic component is introduced into the reaction vessel and the prepolymer which contains isocyanate groups is added to it. Anionic components which are suitable for incorpora-

tion are, for example the alkali metal salts of amino acids such as taurine, methyltaurine, 6-aminocaproic acid or glycine, sulphanilic acid, diamino-benzoic acid, ornithine and lysine and 1:1 addition products of sultones such as propanesultone or butane sultone with diamines such as ethylene diamine, hydrazine or 1,6-hexamethylene diamine.

Compounds which are particularly suitable for the incorporation of cationic groups are, for example, those which contain hydroxyl and/or amino groups that are reactive with NCO groups and which in addition have at least one basic nitrogen atom which can be converted into the salt form with acids or alkylating agents before or after reaction of the compound with isocyanates. Suitable starting materials for the preparation of cationic polyurethane dispersions are mentioned e.g. in German Offenlegungsschrift No. 1,595,602.

The incorporation of ammonium groups may, however, also be carried out for example by the action of a tertiary amine in a polyurethane which contains chlorine or bromine atoms which are capable of being alkylated. Sulphonium or phosphonium groups may also be introduced in an analogous manner.

Quaternary ammonium groups may also be introduced by means of chain lengthening reactions involving the use of halogenated monohydric alcohols, tertiary amino monoalcohols, polyhalides and polyamines, as described in Belgian Patent Specification Nos. 639,107 and 659,026.

The dispersions are generally adjusted to a solids content of 20 to 60% by weight, preferably 30 to 50% by weight.

The polyurethane dispersions are stable and can be stored and transported and may be blended with polymer dispersions and copolymer dispersions based on vinyl acetate, butadiene, styrene, acrylonitrile, acrylic acid esters and methacrylic acid esters, vinyl chloride, vinylidene chloride and other polymerisable and copolymerisable monomers and modified in known manner, mixed with other blending components, fillers, cross-linking agents and other additives before being used to impregnate the fleeces.

The polyurethane dispersion described below, for example, may be used for the process according to the invention:

212 g of a polyester of adipic acid, 1,6-hexanediol and neopentylglycol are dehydrated under vacuum (water pump) at 120°C. for 30 minutes and then reacted with 38 g of 1,6-hexanediisocyanate for 2 hours. After cooling, the melt is taken up in 700 ml of acetone, and a solution of 50 g of water, 3.75 g of ethylene diamine, 7.6 g of 1,3-propanesultone and 35 g of 10% aqueous sodium chloride solution is added. After a short reaction time, 310 ml of water are stirred in rapidly and the acetone is distilled off under vacuum (water pump). The 40% disper-

sion obtained can be used directly for the process of the invention. The products of the process are produced in a simple manner without a large number of individual process steps and may be used as synthetic leathers which have a very smooth surface and excellent wearing properties.

A suitable apparatus for producing imitation leather according to the process of this invention is shown in the accompanying drawing. A reaction mixture is applied to a temporary support (1) from a mixing gear (2). After the mixture begins to solidify a non-bonded fibre fleece (3) is introduced from above. Its direction is adjusted by roller (4) and it is placed on the partially solidified polyurethane layer (5). From the mixing gear (6) a polymeric binder is introduced into the fleece and distributed by means of roller (7). After passing under a heating means (8) the product is removed from the temporary substrate (1) and if necessary dried in a heating chamber (9). The apparatus may also comprise means for applying a leather finish to the temporary support e.g. roller (10), rotating brushes or a spraying device. The resulting imitation leather is finally rolled up (11) and then ready for use.

The following Examples illustrate the invention. In these all parts and percentages are by weight unless otherwise stated.

#### Example 1

A  
1500 g of ethylene glycol polyadipate (OH number 56) and 376 g of ethylene glycol polyadipate (OH number 178) are dehydrated for one hour at 13 mm Hg and 110°C., and 485 g of a mixture of 65% of 2,4- and 35% of 2,6-tolylene diisocyanate are then added and the whole reaction mixture is stirred for 40 minutes at 110°C. A prepolymer having an NCO content of 4.85% (calculated 4.95%) is obtained.

115 g of this prepolymer were dissolved in 90 ml of chlorobenzene, 255 ml of xylene and 12 g of dimethylformamide at 100°C., a hot solution of 12 g of 4,4'-diaminodiphenylmethane in 10 g of xylene was added and the mixture was stirred for 8 seconds and then poured out on to a hot glass plate. After 30 seconds, a stitched fibre fleece of 45% Perlon, (Perlon is a Registered Trade Mark) 10% regenerated cellulose and 45% polyethylene glycol terephthalate was placed on this film and light pressure was applied. Polyaddition was then completed at 100°C. with evaporation of the solvent, and the product was stripped from its support.

B  
20.3 g (280 cm<sup>2</sup>) of the product of Example 1A was impregnated with 30 g of a 60% polyisobutylene dispersion in 20 g of



water. The finished product contained 68% of polyisobutylene. It was able to withstand 200,000 flexures without damage and was found to have a permeability to water vapour of 0.5 mg/hcm<sup>2</sup> (IUP 15; see "Das Leder" 12 (1961), 85-88).

## C

55.7 g (680 cm<sup>2</sup>) of the product of Example 1A were impregnated with 100 g of a 41% aqueous dispersion of a polymer based on butyl ethyl acrylate. After drying at 100°C., the bonded product contained 65% of this polymer; it was able to withstand 200,000 flexures in the Bally-Flexometer and had a permeability to water vapour of 0.6 mg/hcm<sup>2</sup>.

## D

60.3 g (700 cm<sup>2</sup>) of the product of Example 1A were impregnated with a mixture which had the following composition.

60 ml of decalin were emulsified in 50 g of a 48% dispersion of an acrylonitrile butadiene polymer containing 4% methacrylic acid and 50 g of a 38% anionic polyurethane dispersion (from a neopentyl glycol/hexamethylene glycol polyadipate, hexamethylene-1,6-diisocyanate and water as chain lengthening agent and the addition product of ethylene diamine and propane sultone) by stirring at the rate of 1300 revs/min to produce a reverse emulsion. After impregnating and drying at 80°C., an imitation leather product was obtained which was able to withstand 200,000 flexures in the Bally Flexometer without damage and which was found to have a permeability to water vapour of 0.9 mg/hcm<sup>2</sup>.

## Example 2.

152 g of a partly branched ethylene glycol polyadipate (OH number 59) and 24 g of bis-(β-hydroxyethoxy) benzene-1,4 are dissolved in 300 ml of xylene and 20 g of dimethyl formamide together with 3 g of Solvent Black 27 at 100°C. 50 g of 4,4'-diisocyanatodiphenylmethane in 60 ml of hot xylene were introduced into this solution with stirring, 0.6 g of diazobicyclo-octane was added and the reaction mixture was stirred for 10 seconds and then poured out on to a hot, polished VA steel plate. After 30 seconds 29.1 g of a stitched fleece of 70% Perlon, 20% bifilar Perlon and 10% regenerated cellulose was placed on this reaction mixture which was then thoroughly heated at 100°C. Without stripping the product from its support, it was impregnated with 120 g of a 26% dispersion of a butadiene-acrylonitrile polymer with 4% methacrylic acid which also contained a heat sensitizing agent according to French Patent Specification No. 1,381,822 and 2% of dispersed carbon black and to which 1% (based on the polymer) of an aqueous silicone emulsion had been added. The pro-

duct was coagulated by heating to the coagulation point (41°C.) and the water was evaporated off at 120°C. A bonded imitation leather product was obtained which had a permeability to water vapour of 1.8 mg/hcm<sup>2</sup> and was able to withstand 200,000 flexures in the Bally Flexometer.

## Example 3

In a manner analogous to Example 2, an identical fleece was placed on the same reaction mixture as polymeric layer. The substrate was in this case a siliconized separating paper which had been embossed with a buffalo grain and on which a cationic polyurethane dispersion coloured black with carbon black had been applied in a thickness of about 5 to 10 μ as a finish before application of the covering layer.

After the reaction mixture had reacted, the fleece was impregnated with 100 g of a polyurethane dispersion as in Example 1D and thoroughly heated. By stripping the product from the separating paper, an imitation leather was obtained which had a permeability to water vapour of 1.1 mg/hcm<sup>2</sup>, was able to withstand 200,000 flexures in the Bally Flexometer and a hot abrasion test according to Satra (see Pittard, Jour. Soc. Leather Trade Chem. 4, pages 20-125) and a hot ironing test at 150°C. without damage. By virtue of the hydrophilic character of the binder it was capable of absorbing 3.5% of its own weight of water vapour in the course of 6 hours at a relative humidity difference of 65% to 86%. (For comparison it may be mentioned that split leather under the same conditions can absorb about 10% but commercially available imitation leather less than 1% (Corfam), (Clarino) or approximately 2% (Xylcne). (Corfam, Clarino and Xylene are Registered Trade Marks).

## Example 4

670 g of a polypropylene glycol ether (OH number 58) were reacted after dehydration with 122 g of a mixture of 65% of 2,4- and 35% of 2,6-tolylene diisocyanate for 40 minutes at 110°C., to produce a prepolymer having an NCO content of 3.8%.

66 g of this prepolymer were dissolved in 10 g of dimethylformamide and 240 ml of mineral spirit (aliphatic hydrocarbon mixture boiling in the range of 160°C. to 196°C.) at 100°C., and 0.4 g. of a triturated Pigment Yellow 3 (C.J. 11 710) in a polyalkylene adipate was added. A hot solution of 6 g of 4,4'-diaminodiphenylmethane in 9 g of xylene was added at 100°C. and the reaction mixture was stirred for 2 seconds and then poured out on to a hot glass plate which had previously been covered with an acrylate finish. After a further 3 seconds, a stitched fleece of 100% polyethylene glycol terephthalate was pressed on to the covered glass plate and the poly-

addition reaction was completed at 100°C. with evaporation of the solvent.

5 The fleccc was then impregnated with a 40.6% dispersion of a copolymer of ethyl acrylate and a small amount of acrylic acid and dried. The resulting finished imitation leather had a permeability to water vapour of 1.6 mg/hcm<sup>2</sup>.

10 One part of the imitation leather was treated with a lacquer finish suitable for leather, using a casting machine. This part had a permeability to water vapour of 0.3 mg/hcm<sup>2</sup>.

#### Example 5

15 A man's boot-upper was prepared from two-coloured embossed grain leather in a conventional way. First the 4 parts of such a boot-upper namely the vamp, the extended vamp and the quarters were punched out of a leather sheet using punching knives. The parts were then primed, perforated, a decorative seam was stitched in, and then the parts were edged and assembled in the usual way. The finished boot-upper was fixed onto a metal plate and a layer of catalyst activated commercially available silicone paste was applied to the metal plate by a doctor blade. The layer was about 5 mm thick. On top of this layer a textile fabric was placed and the assembly was left to stand at room temperature for 10 hours. After this time the silicone paste had hardened and the silicone rubber matrix of the boot-upper thus formed was carefully removed.

35 The matrix thus formed was used as the temporary support for making a boot-upper out of imitation leather. The procedure was as follows:

40 700 g of diethylene glycol polycarbonate (OH number 62; corresponding to 785 m mols of OH) were dehydrated in the vacuum at 110°C and then mixed with 137 g of toluene diisocyanate (65% 2,4 and 35% 2,6 isomer) at 110°C. and stirred for 40 minutes. An NCO prepolymer having 3.26% NCO was formed.

50 60 g of dimethyl formamide and 200 g of toluene were added to 520 g of this NCO prepolymer. In a second vessel a solution was prepared of 40 g 4,4'-diaminodiphenyl methane in 50 g of dimethyl formamide and 300 g of toluene. This solution was treated with 0.5 g of solvent black 1 and 10 g of a carbon pigment black dispersion in a polyester. By means of a geared pump 144 g of the prepolymer solution and 80 g of the amine solution were pumped into a mixing head intimately mixed and sprayed onto the matrix. Within 15 seconds split leather is applied to the sprayed matrix and the assembly heated thoroughly for 8 minutes at 80°C. The coated split leather is then removed and dried for 10 minutes. The result is a coated split leather. This material already has the contours

65 of a man's boot on its surface including the decorative seam, the perforation and so on.

70 Test specimens were taken from this leather and it was shown that the material was undamaged after 200,000 flexures in the dry state, 100,000 flexures in the wet state and 10,000 flexures at -15°C. in a Bally Flexometer. After 5 weeks' storage at 70°C. and 95% relative humidity 200,000 flexures in the Bally Flexometer were possible without damage to the material.

75 A coating made in the same way without applying it to a split leather had a tensile strength of 200 kp/cm<sup>2</sup>, and elongation at break of 500% and a tear resistance of 32 kp/cm.

#### Example 6

80 1600 g of polypropylene glycol ether (OH number 56) are dehydrated as described above and reacted with 400 g of 4,4'-diisocyanatodiphenyl methane to a prepolymer with 3.32% of NCO. 6.3 g of 4,4'-diaminodiphenyl-2,2-propane in 20 g of toluene are added at 60°C. to 76.2 g of this prepolymer in 20 g of toluene and 25 g of cyclohexanone.

90 The solution is applied by means of a doctor blade after stirring for 10 seconds to a silicone matrix with a kid leather grain, applied after 15 seconds to split leather and dried at 60°C. A coated leather is produced which survives 200,000 flexures in the Bally Flexometer without damage.

#### Example 7

100 As in Example 5 an 85% solution of a prepolymer was prepared from 4,040 g of a butane diolpolyadipate (OH number 64) and 1,140 g of 4,4'-diisocyanatodiphenyl methane in 5,180 g of perchloro-ethylene. 896 g of this prepolymer was mixed as above with 40 g of 4,4'-diamino-diphenylmethane in 150 g dioxane at 100°C. The solution was sprayed onto a silicone separating paper which had been previously covered with a cationic polyurethane dispersion finish (to which an aqueous carbon black trituration had been added) (see D. Dieterich loc. cit.) and a fabric applied. The mixture was likewise sprayed onto glass, metal or Teflon and a bonded fleece or buffed grain leather then pressed on. Coated specimens were obtained which survived 200,000 flexures in the Bally Flexometer without damage. Films of this mixture (without substrate) have tensile strength of 400 kp/cm<sup>2</sup>, breaking elongation 500% and tear resistance of 60 kp/cm.

#### Example 8

120 57 g of partly branched diethylene glycol polyadipate (OH number 63) and 5.1 g of 2,5-dichloro-1,4-diamino benzene are dissolved in 20 g of toluene at 60°C. 16.2 g of 4,4'-diisocyanatodiphenyl methane were added and the mixture stirred for 10 seconds, poured

onto glass, fabric applied and dried at 60°C. The coated fabric could be bent 200,000 times in the Bally Flexometer without damage.

#### Example 9

- 5 35.4 g of a partly branched ethylene glycol polyadipate were dissolved with 3.5 g of hexanediol-1,6 in 30 g of acetic acid at 60°C. 6 g of a commercially available carbon black trituration in polyester were added. 19.6 g of a liquid mixture of reaction products consisting of 4,4'-diisocyanatodiphenyl methane with propylene glycols were mixed with 0.2 g of a catalyst on a silamorpholine basis stirred for 8 seconds, applied to a glass plate by means of a doctor blade, split leather applied after 30 seconds and removed after 40 minutes. A finished imitation leather was obtained with the appearance of patent leather which survived 200,000 flexures at room temperature and 10,000 at -25°C without damage.

#### WHAT WE CLAIM IS:—

1. A process for covering a fibrous web with a polymeric coating comprising the steps of:—

- 25 a) applying to a temporary support a layer of a reaction mixture which comprises (1) at least one polyisocyanate and (2) at least one compound containing active hydrogen atoms and which will undergo a polyaddition reaction with the polyisocyanate to form a microporous polyurethane (urea) layer,
- 30 b) applying to the layer, before the polyaddition reaction is complete, a fibrous web, and
- 35 c) removing the fibrous web with the adhering polymeric layer from the temporary support.

- 40 2. A process as claimed in claim 1 in which the fibrous web is split leather, grain leather, suede or a knitted or woven fabric.

3. A process as claimed in claim 1 in which the fibrous web is a fibre fleece.

- 45 4. A process as claimed in claim 3 in which after the fibre fleece has been applied to the layer the fleece is impregnated with an aqueous solution of a polymeric binder and the binder is coagulated, the amount of binder used being 10 to 98% by weight based on the weight of the fibre fleece.

- 50 5. A process as claimed in claim 3 or claim 4 in which the fleece is applied so that it penetrates 1 to 80% of the thickness of the layer.

- 55 6. A process as claimed in claim 5 in which the fleece penetrates 10 to 30% of the thickness of the layer.

- 60 7. A process as claimed in any of claims 3 to 6 in which the fleece used is of polyester, polyamide, polyacrylonitrile, polyvinyl chloride, polyvinyl acetate, polyvinyl alcohol,

rayon, cotton, collagen, polyurethane and/or regenerated cellulose fibres.

8. A process as claimed in any of claims 4 to 7 in which the polymeric binder comprises polyurethane.

9. A process as claimed in claim 8 in which the binder comprises 10 to 100% of polyurethane.

10. A process as claimed in any of claims 4 to 7 in which the polymeric binder is a polyurethane which is an anionic polyaddition polymer.

11. A process as claimed in any of claims 4 to 9 in which 10 to 100% of the polymeric binder is an acrylonitrile-butadiene or chloroprene polymer.

12. A process as claimed in claim 11 in which the polymeric binder comprises methacrylic and/or acrylic acid.

13. A process as claimed in any of claims 1 to 12 in which the reaction mixture comprises (1) at least one polyisocyanate (2) at least one compound containing NH and/or OH groups which will react with NCO groups and having a molecular weight of at least 500 and (3) at least one chain lengthening agent which has a molecular weight of below 500 and contain NH and/or OH groups which will react with NCO groups.

14. A process as claimed in claim 13 in which the three reactants (1), (2) and (3) are mixed together in a single stage process.

15. A process as claimed in claim 13 in which the reactants (1) and (2) are reacted together in a first stage to give a prepolymer which is, in a second stage, mixed with the chain lengthening agent.

16. A process as claimed in any of claims 1 to 15 in which the polyaddition reaction is carried out in solvent which is a non-solvent for the polyurethane (urea) produced.

17. A process as claimed in claim 16 in which step (b) is carried out while the layer still contains not more than 50% of the original quantity of solvent used.

18. A process as claimed in any of claims 1 to 17 in which step (b) is carried out within a time, after the reactant in the reaction mixture have been mixed, which is up to 300 times the reaction time (as herein defined) of the reaction mixture.

19. A process as claimed in claim 18 in which step (b) is carried out in a time within 15 to 50 times the reaction time.

20. A process as claimed in any of claims 1 to 19 in which the temporary support has been coated with a finish before the layer of reaction mixture is applied, which finish will adhere to the polymeric coating and be removed in step (c) from the temporary support.

21. A process as claimed in claim 1 substantially as herein described.

22. A process as claimed in claim 1 sub-

stantially as herein described with reference to any one of the Examples.

23. Fibrous webs when provided with a polymeric coating by a process as claimed in any of claims 1 to 22.
- 5 24. Products as claimed in claim 23 which are leather substitutes.

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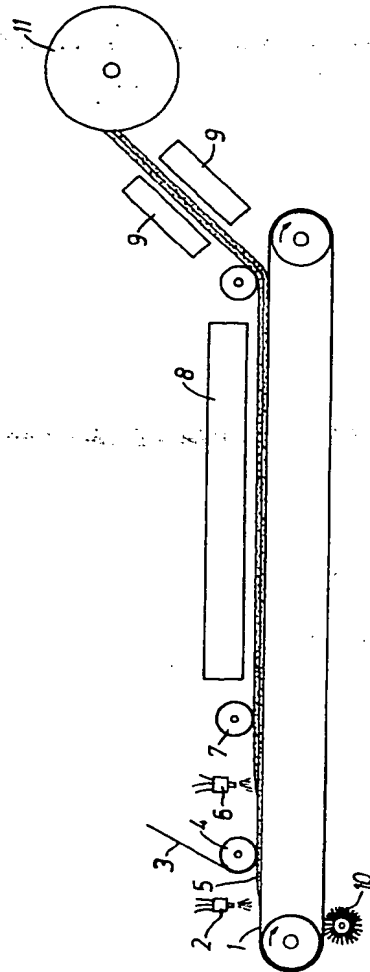
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